Appendix A: Colorado School of Mines, Materials Research Science and Engineering Center in Renewable Energy

**Renewable Energy Materials Research Science and Engineering Center**
**Colorado School of Mines**
**CHECRA Grant: $400,000 (per year for 6 years)**

**Summary:** The Materials Research Science and Engineering Center (MRSEC) at the School of Mines, under the leadership of Dr. Craig Taylor, is focused on investigating emerging renewable energy materials, such as enhancing solar panels through nanotechnology and improving membrane technologies important to renewable energy applications, such as batteries, fuel cells and electrolyzers.

**Description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity**

With annual global energy consumption expected to increase to as much as 30 terawatts by 2050 and mounting concerns over oil reserve depletion, energy security, and global warming, meeting world energy demand will be one of the grand challenges of the 21st century. While renewable and alternative technologies have the potential to address the most serious concerns with fossil fuels, cost is a major obstacle to their widespread deployment. There has been remarkable progress, for example, in lowering the price of photovoltaic (PV) electricity generation, yet present costs are nearly ten times higher than electricity produced from coal. Similar price differentials exist when comparing fuel cells with conventional electricity generators. Estimates based on historical trends give several decades before many renewable technologies become competitive. Transformative technological innovation is the key to accelerating this time line and fundamental advances in materials science will spearhead this process.

The MRSEC consists of two Interdisciplinary Research Groups (IRGs). IRGI is concentrating on materials of potential use in the next generation of PV devices, but the scope of this IRG will be much broader since the systems of interest have important properties in common with a wide range of other electronic and opto-electronic materials. The important questions this IRG is attempting to answer involve the scattering and relaxation mechanisms that govern electronic transport in semiconducting materials of use in PV applications, especially mechanisms that are altered in nanostructured environments. These nanostructures include quantum wires and quantum dots, which have potential for significant improvements in efficiency by tuning the optical and electronic properties through size, composition, and surface termination, and by uniquely quantum mechanical effects, which offer possibilities for collecting solar radiation that is lost in conventional cells. The long-term research directions of this IRG are aimed at producing transformative changes in PV technology through significant improvements in materials properties that result from development of fundamental concepts for more efficient carrier generation and collection.

The second Group (IRG2) is concentrating on advanced membranes for renewable energy applications, with the scope being also much broader since the systems to be studied include polymers, ionic solids, and hybrid systems. Solid electrolyte materials and membrane technologies are central to many processes in the conversion, utilization, and storage of energy. Very frequently, ionic transport is the "weak link" in electrochemical energy storage or conversion systems. At present, the myriad interactions that occur in ion transport membranes- ion-ion, ion-solvent, and ion-electrode-are poorly understood. Fundamental research is crucially needed to provide the knowledge required for the intelligent design of novel transport membranes with highly optimized properties. IRG2 is fabricating novel transformative ion conducting materials by synergistically combining materials with dramatically different ionic transport characteristics.

An additional research group involves the evaluation of clathrate structures as potential materials for renewable energy applications, such as hydrogen storage, photovoltaics, and membranes for ionic transport. Energy storage, and in particular storage of hydrogen or methane produced from renewable resources, is another area of research in renewable energy where transformative research is critical. Clathrate hydrates, with as much as 164 volumes of gas contained per volume of clathrate hydrate, present a potentially attractive class of energy storage compounds. Center scientists and engineers have succeeded in making silicon clathrate materials in larger volumes for our experiments in using these materials in solar cells.

In addition to the two research groups, funds were used to support "seed" grants on promising but very preliminary research projects. Six projects funded in 2013 were entitled: (l) Development of Robust Hybrid Polymer Membranes with Membrane-Protein-Mediated, Light- Driven Proton Transport Performance, (2) Inorganic Clathrates for Renewable Energy Applications, (3) Nonstoichiometric Oxides for Solar Thermochemical Fuels Production, (4) Development of Electrochromic Thin Film Transistors and Dichalcogenides for Sustainable $H_2$ Production, (5) Quantum Dot Metamaterials, and (6) Electrochemical-Mechanical Force Coupling at Nano- and Micro-Scales in Lithium Intercalation Compounds

| Principal Senior Investigators | Funding from CHECRA |
|---|---|
| P. Craig Taylor, Director | $40, 000 |
| Reuben Collins, Associate Director and Head | $120,000 |
| IRG 1 Andrew Herring, Head IRG2 | $120,000 |
| Carolyn Koh, Head, Seed Grant Program and Head IRG3 | $120,000 |

**The manner in which each principal person or entity applied the funding in connection with the project**

P. Craig Taylor: Discretionary funding of promising new research directions.
Reuben Collins: Funding for films of silicon nanodots imbedded in an amorphous silicon matrix for improved solar cell materials
Andrew Herring: Funding for organic-inorganic nanostructured membranes for fuel cell and battery applications
Carolyn Koh: Funding of novel approaches to new materials for photovoltaic applications or membrane technologies. Funding for development of clathrate materials for renewable energy applications.

**Results achieved**

Center scientists and engineers have developed a novel hybrid nanocrystalline silicon – amorphous silicon deposition system has been designed, assembled, installed and is now in operation. By decoupling crystal silicon nanoparticle and amorphous silicon depositions, engineered nanocrystalline silicon films can be grown with unprecedented control of silicon nanoparticle size, crystallinity, surface termination, density, doping and distribution, as well as complete control of amorphous matrix to the point of allowing an entirely different amorphous matrix (e.g. amorphous silicon-carbon) to be integrated with high quality silicon nanoparticles. The system is unique within the nano materials community depositing structures with properties tailored specifically to understanding and harnessing hot carrier effects in crystalline silicon nanoparticle – amorphous silicon hybrids.

Center scientists and engineers have also developed a predictive model of hybrid nanocrystalline silicon – amorphous silicon hybrids. The model demonstrates that silicon quantum dots can be quantum confined in an amorphous silicon matrix. The confinement is found to be fundamentally different from conventional heterojunction systems. It is in part a topological confinement with both materials primarily made of the same constituent, silicon. The confinement primarily occurs in the valence band. There is a minimum nanoparticle size of ~2 nm for confinement, a feature unique to amorphous confinement, and an associated band gap of ~1.3 eV. Below this size, the electrons in the system are more likely to be in localized states of the amorphous silicon matrix and the material will behave like conventional amorphous silicon. Using the theoretically predicted electronic structure, an atomistic relaxation and transport simulator has been developed which allows excited state decay, hot carrier transfer, and equilibrium transport all to be analyzed within the same computational framework. Results from this simulator will provide microscopic rates to be included in predictions of macroscopic materials properties like mobility, lifetime, and photovoltaic efficiency.

The hybrid nanocrystalline silicon – amorphous silicon growth process was optimized to produce very compact films of highly crystalline silicon nanoparticles with sizes from 3 to 7 nm. Using computational fluid dynamics modeling a phase diagram was developed providing the first in depth understanding of the connection between pressure, flow rate, residence time, and nanoparticle size and crystallinity. Using these results, the first of their kind superlattice structures have been deposited and characterized. Interaction of the amorphous silicon and nanocrystalline silicon particles is evident, evidence for carrier transfer is observed, and initial devices have been demonstrated. These films form the basis for fundamental studies of hot carrier effects, and for devices harnessing these effects.

Through integrated theory and experiment, Center scientists and engineers have transformed our understanding of ion transport in novel nanostructured systems utilizing nanoionic effects. The team has produced new proton ionic conductors with enhanced stability and record conductivity by manipulating interfacial phenomena in both mixed-phase ceramic and phase-separated polymeric systems. In the case of the polymeric system the nexus of theory, synthesis, and characterization has produced membranes that perform well under low hydration and elevated temperature. At a molecular level the combined computational and experimental approach has resulted in an enhanced understanding of how acids interact with the solvent in the proton exchange membranes. Center scientists and engineers have found that the addition of heteropoly acids generally decreases the membrane's uptake of water and reduces the diffusion coefficient of water while enhancing the proton conductivity. At a molecular level this occurs due to the waters and protons shifting location. This could decrease the diffusion coefficient and at the same time facilitate the formation of a hydrogen bonding network, and bring about morphological change. To study the bridging effect Center scientists and engineers have adopted molecular dynamics simulations and small angle x-ray scattering experiments to investigate the effects on film morphology at various hydration levels. Center scientists and engineers have found excellent agreement between the spacing of ionic domains calculated from x-ray results and the percentage of large ionic domains (>15 Å) computed from simulated pore size distributions.

To further elucidate the transport phenomena Center scientists and engineers have compared the measured conductivity with the calculated conductivity. The difference between them shows the contribution of proton transport. It is well known that a hydrogen bonding network is essential for proton transport, therefore a more interconnected hydrogen bonding network has greatly improved the proton conductivity.

The successful combination of both experiment and theory has also led to combined efforts in other areas of doped polymer systems. Extensive high level calculations in addition to experiments have confirmed the oxidation state of the cross-linked polymers. These basic studies have now transitioned to more applied research and development at 3M Corporation.

In the case of the mixed-phase ceramics, Center scientists and engineers have developed large-grained electrolytes with uniquely-passivated grain boundaries using a new approach to perovskite synthesis utilizing solid-state reactive sintering in the presence of appropriate additives. These additives enhance sintering and grain development and under reducing conditions can lead to unique nanocomposite systems with exceptional conductivity. This approach, substantiated by theory, has yielded nano-composite perovskite oxides with record-setting proton conductivity at temperatures below 400 °C. This breakthrough provides a new strategy to overcome the classic grain-boundary resistance limitation frequently encountered in polycrystalline solid-state ion conductors, and opens to door to the commercial deployment of these materials in lower-temperature applications. The discovery has also been transitioned to research and development at a ceramics company (CoorsTek) for use in fuel cell and membrane reactor devices and has catalyzed a DOE-sponsored project on nanoionic interfaces at NREL to apply these concepts in other areas. In concert with these experimental discoveries, the Center scientists and engineers have developed density-functional theory investigations to yield a critical understanding of the effect of defect and dopant interactions on proton conductivity both in the bulk and at surfaces or grain boundaries in perovskite proton conductors at the atomic scale. These studies have yielded a new design strategy to increase proton conduction performance in these materials by selecting complementary dopant and matrix materials on the basis of metal-oxygen bond strengths in order to decrease harmful grain-boundary space-charge effects.

Using atom probe tomography, Center scientists and engineers have, for the first time, obtained direct atomic-scale confirmation of the space charge layer theory at ceramic grain boundaries. This breakthrough result confirms the scientific theory that the increased grain boundary resistance observed in these ceramics is due to oxygen ion depletion in the core of the grain boundary. The results also provide quantitative values for the height and width of the space charge layer at the grain boundary.

Finally, in the last year Center scientists and engineers have been able to use our growth technique to fabricate complete fuel cells, demonstrating some of the highest power densities ever reported for a ceramic fuel cell. Our fuel cell is constructed from the state of the art proton conductor as an electrolyte, a cermet as an anode, and another ceramic as a cathode for high-performance, intermediate temperature operation. The fuel cell also shows highly promising performance when operated on methane.

Center scientists have been able to produce large quantities (grams as opposed to milligrams) of an open cage (clathrate) structure that is made from silicon. Originally, these clathrate silicon materials were being used to test how much hydrogen could be stored and how easily it could be extracted. Currently Center members are making larger samples of silicon and silicon- germanium clathrates and testing them as materials for solar cell applications. In particular theoretical calculations indicate that these forms of silicon an silicon-germanium exhibit direct optical band gaps, which means that they absorb light much better than the diamond silicon structure that is commonly in use for today's solar cells.

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**Education and Outreach - Partial CHECRA Support**

None

Appendix B: University of Colorado, Liquid Crystal Materials Research Center

*Liquid Crystal Materials Research Center*

*University of Colorado – Boulder*

*CHECRA Grant: $400,000 (per year for 6 years)*

SUMMARY

The Liquid Crystal Materials Research Center (LCMRC or the Center) has existed on the University of Colorado – Boulder campus since the early 1980s, with block funding from the NSF Division of Materials Research since September 1998. The LCMRC is currently funded as an NSF Materials Research Science and Engineering Center (MRSEC), one of an elite national network of advanced materials research programs.

*DESCRIPTION OF THE PROJECT, THE PRINCIPAL PERSONS OR ENTITIES INVOLVED IN THE PROJECT*

A major theme of materials science as we enter the 21st century is understanding and manipulation of the interactions between self-organizing complex molecules. It is precisely here that the study of liquid crystals has the greatest impact. Nowhere else are the requirements for understanding the delicate interplay between molecular architecture and its macroscopic manifestations more demanding than in the directed design of liquid crystals.

The Liquid Crystal Materials Research Center is one of the principal centers of liquid crystal study and expertise in the world, its research spanning the range from cutting-edge, basic liquid crystal and soft materials science to the development of enhanced capabilities for commercially important electro-optic, nonlinear-optic, chemical, biological, and other novel applications. The Center is a unique venue worldwide for research on key aspects of liquid crystal science and technology, chief among these the science and application of ferroelectric liquid crystals. The core Center research program is at the University of Colorado, Boulder.

The Center's research is organized within an Interdisciplinary Research Group addressing three major project themes: 1) understanding the relationship between molecular structure and macroscopic materials structure and properties of liquid crystals; (2) inventing new and useful ways of controlling liquid crystal behavior through interaction with surfaces; and (3) inventing and exploring new polymer materials possessing unique properties deriving from liquid crystallinity. Each of these research themes integrates *molecular modeling and design, chemical synthesis, physical studies,* and *applications development* into a multidisciplinary, collaborative research effort.

In 2013, the CHECRA funding was allocated to the three focus areas of the center described in this summary – research, industrial outreach, and education outreach.

Appendix B: University of Colorado, Liquid Crystal Materials Research Center

*FUNDING ALLOCATED TO EACH PRINCIPAL PERSON OR ENTITY*

### *Research*

The past year of MRSEC, with NSF funding supplemented by the CHECRA matching state funds, has continued in its role as CU Boulder's single most visible materials research group nationally and internationally. Highlights of CHECRA funding published in the most prestigious journals, include discovery of a new heliconical nematic phase of bent molecular dimers, appearing in *Proceedings of the National Academy of Sciences* and *Physical Review Letters*, discovery of ferromagnetic liquid crystals, submitted to *Proceedings of the National Academy of Sciences*, and observation of liquid crystal ordering around topologically complex knots, appearing in *Nature Materials*. A summary of major research themes is a s follows:

•*Helical Nanofilament (HNF) Phases* – The HNF phase is perhaps the most complex and unique soft materials system known. While the basic story around the structure of HNF phase, as described by the LCMRC in 2009, is understood, many key questions and opportunities remain outstanding. This phase represents perhaps the most complex hierarchical self-assembly in the LC space, and has potential applications in molecular electronics and photovoltaics.Here we address: (i) - *The HNF phase as a nanoconfinement medium* - Freeze-fracture transmission electron microscopy reveals that the twisted layer structure of the bulk HNF phase as an array of filaments. While the filaments are packed they exhibit interstitial spaces that are of few nanometer dimension which we have demonstrated are effective chiral nanoconfinement spaces. A wide variety of organic guest materials can be nanoconfined by the filaments. (ii) - *Meso-scopic Diastereomericity* - We have pursue our recent discovery of a dramatic difference between the alignment states of a chiral guest in HNF domains of different handedness, a long sought mesoscale chiral surface interaction. (iii) *A Modulated Helical Nanofilament Phase* – Until recently the HNF phenomenon seemed to be limited to mesogens possessing the benzylideneaniline (Schiff base) moiety. Over the past two years, we have discovered and characterized a new HNF phase, as evidenced by FFTEM, composed of simple alkoxybiphenylcarboxylate units and lacking benzylideneanilines. Detailed analysis of data, most importantly XRD of powder samples, and FFTEM of lamellar preparations (formed close to glass surfaces), prove that this phase of the biphenyl mesogens is actually a new phase, a modulated HNF phase ($HNF_{mod}$) exhibiting a yet more complex hierarchical self assembly than the "simple" HNF. Related mesogen molecules of the series **1** pack into twisted layers with negative Gaussian curvature, which then stack to form HNFs. This behavior is similar to that observed by the classic HNF phase, with the addition of a modulate parallel to the layers observed by XRD and FFTEM. While the layers in the $HNF_{mod}$ homologues expand with the molecular length as expected, the second modulation has the same metrics (~40Å) for all homologues.

•*Liquid Crystals of Nanoscale DNA* – Using complete enantiomers of natural nanoDNA oligomers, i.e. DNA oligomers made with L-ribose instead of D-ribose obtained from NOXXON Pharma AG we have been able to study the role of chirality in the aggregative behavior of nanoDNA duplexes, in particular to explore the nature of mixing of enantiomers in D,L mixtures. We find that in columnar phases of blunt end duplexes the columns are heterochiral, but are homochiral if there are complementary overhangs between the duplexes. Ongoing research will focus on obtaining LC phases in oligomers shorter than 4 bases, and obtaining nonenzymatic ligation of nanoDNA oligomers in the LC phases.

•*Heliconical Nematic Phase Experiment and Theory* – Our discovery of the TB phase structure opens a new branch of liquid crystal science which we propose to advance on a variety of experimental and theoretical avenues: (i) *Study of the dependence of the TB helix on molecular architecture*, starting with the variation of spacer length n in the BCnCB series. (ii) *Study of mixtures with typical bent-core molecules* forming spontaneously polar and chiral smectic phases to explore the conditions for the onset of layer ordering in the TB nematic. (iii) *Atomistic molecular dynamic computer simulations* as a means to explore in detail the intermolecular interactions and correlations giving rise to the TB phase. (iv) *Microrheology of the TB phase* - The TB is a completely novel phase with respect to its macroscopic hydrodynamic and viscoelastic behavior. Qualitative observation shows extreme shear thickening behavior. (v) *Nonlinear Smectic Elasticity of the Helical State in Liquid Crystals and Helimagnets* - The low-energy elasticity of a twist-bend nematic liquid crystal and of a Dzyaloshinskii-Morya (DM) spiral state in a helimagnet with negligible crystal symmetry fields (e.g., MnSi, FeGe) should both be identical to that of a smectic liquid crystal, thereby inheriting its rich phenomenology. Starting with an appropriate Frank free-energy of a conical nematic we will develop a transparent derivation of the fully nonlinear Goldstone mode elasticity, which involves an analog of the Anderson-Higgs mechanism that locks the spiral orthonormal (director/magnetic moment) frame to the helical layers. This shows explicitly the reduction of 3 orientational modes of a twisted nematic down to a single phonon mode emerges on scales larger than the pitch.

•*Flexopolydispersity* – Disc-shaped sheets of molecular monolayer clay particles form smectic-like phases which are layered but fail to achieve the quasi-long ranged layer ordering generally found in thermotropic smectics. We are probing this behavior in suspensions of ~1000nm diameter, 2nm thick ZrP sheets which tend to form better smectic ordering when dilute (10%) than when concentrated by centrifugation (50%). The high concentration smectic ordering appears to be compromised by either charge variation on the sheets or by their finite size which introduces a concentration of edge dislocations into the smectic. These questions are being investigated by FFTEM and x-ray diffraction, and by theory of quenched disorder in smectics.

•*Complex-Shaped Elastomeric Particles* – We have demonstrated facile optical manipulation of shape of birefringent colloidal microparticles made from liquid crystal elastomers. Using soft lithography and polymerization, we fabricate elastomeric microcylinders with weakly undulating director oriented on average along their long axes. These particles are infiltrated with gold nanospheres acting as heat transducers that allow for an efficient localized transfer of heat from a focused infrared laser beam to a submicrometer region within a microparticle. Photothermal control of ordering in the liquid crystal elastomer using scanned beams allows for a robust control of colloidal particles, enabling both reversible and irreversible changes of shape. Possible applications include optomechanics, microfluidics, and reconfigurable colloidal composites with shape-dependent self-assembly. Some of these particles have been then incorporated into liquid crystals and used to explore colloidal interactions in liquid crystals.

•*Multiscale Modeling of Self-Assembed Polymer Morphologies* – In collaboration with M. Müller (Göttingen, Germany) we completed investigation of correlations between the structure, dynamics, and mechanical properties of blends comprised of random block copolymers

(RBCPs). Upon increasing the incompatibility between blocks (defined by strength of A-A interaction $e_{AA}$) a gradual formation of microemulsion-like structures were observed. We demonstrated that the self-assembled morphology in the melt gives rise to a viscoelastic transient plateau in the stress autocorrelation function. While an analysis of the entanglement density reveals a slight increase of the number of entanglements in response to microphase separation, the viscoelasticity of the RBCP blend chiefly stems from the slow morphological relaxation and the transient trapping of blocks inside domains. Upon quenching the microphase-separated structure below the glass transition temperature, the shear modulus increases about an order of magnitude compared to the viscoelastic plateau. The structural asymmetry of the segment species gives rise to spatially heterogeneous, local bulk and shear moduli that correlate with local composition fluctuations. The vicinity of a solid substrate that prefers one segment species gives rise to variations of the composition that propagate about 3 molecular extensions into the bulk. In this extended interphase, we observe an oscillatory decay of the composition and the local mechanical properties.

•*Non-Aqueous Lyotropic LCs and Polymers for Battery Applications* – Polymerized lyotropic (i.e., amphiphilic or surfactant) LC (LLC) materials have recently garnered both fundamental and applied interest because their stabilized, ordered, nanoporous structures can be used as unique nanoenvironments for heterogeneous catalysis, molecular size separations (membranes), and enhanced transport. A series of novel symmetrical compounds containing a tris(imidazolium bromide) central core and *n*-alkyl tails at each end containing between one and twenty carbons were synthesized and characterized for thermotropic LC behavior. Imidazolium-containing thermotropic ionic liquid crystals (TILCs) are of interest because of their structural similarity to imidazolium-based ionic liquids (ILs), allowing them to exhibit some IL-like properties in addition to LC order. More imidazolium units is important for increasing IL character; however, the effect of multiple imidazolium units on LC behaviour is not well known. Most reported imidazolium TILCs contain one imidazolium unit; only a handful containing multiple imidazolium units is known. In order to investigate the effect of longer, sequentially linked oligo(imidazolium) cores on thermotropic LC properties, over the past year we successfully synthesized and characterized the thermotropic LC properties of a homologous series of symmetric ionic compounds containing three linearly connected imidazolium salt groups. These new TILCs were based on an alkyl-bridged tris(imidazolium bromide) central core and two peripheral *n*-alkyl tails. Prior work from our group has recently shown that similar compounds containing a bis(imidazolium) central core (i.e., a 'gemini' imidazolium core) produce thermotropic Sm LC phases as confirmed via powder X-ray diffraction (PXRD). The imidazolium components in this new type of calamitic LC motif are chemically similar to imidazolium-based room-temperature ionic liquids (RTILs). Consequently, they should be able to bring RTIL-like functional properties (i.e., ion conduction, enhanced $CO_2$ gas uptake) into the resulting LC phases, as the foundation for a new type of functional thermotropic LC. Encouraged by these initial results, over the past year, we successfully synthesized and characterized the LC behavior of tris(imidazolium bromide) analogues that contain more imidazolium RTIL-like units per molecule, in order to determine the effect of the expanded ionic core structure initially on LC behavior and later on the functional properties of the materials Out of the 10 homologues synthesized with an even number of carbons in the alkyl tails, only the three containing the longest tails (i.e. 16-, 18-, and 20-carbon tails) exhibited thermotropic mesomorphism. These three homologues all form a SmA phase upon heating from the crystalline state and initial annealing at 160 °C. The two homologues with the longest *n*-alkyl tails (i.e. 18 and 20 carbons) in the series were also found to form an additional, as-yet unidentified, higher-order SmX phase that appears below the SmA phase in temperature. It was observed that the length of the peripheral *n*-alkyl tails had to be at least the length of the entire poly(ion) core in order to induce thermotropic LC phase formation. In general, as the length of the *n*-alkyl tails in these homologues increased, the $d_{100}$ spacing of their SmA and SmX layers decreased, suggesting a tendency for more tail interdigitation between the layers with increasing tail length.

*Liquid Crystal Reorientation Induced by Aptamer Conformational Changes* – The extraordinary physical properties of liquid crystal (LC) materials – long-range orientational order, responsiveness to external stimuli, and optical anisotropy – have inspired liquid crystalline based sensing applications. Aptamers, nucleic acids that specifically bind ligands (e.g. small organic molecules, metal ions, and proteins) with high affinity are a promising molecular probe for highly multiplexed bio-sensing applications. We have demonstrated that aptamer-ligand binding events, involving adenosine or arginine, at a cationic surfactant-laden aqueous/liquid crystal (LC) interface trigger a LC reorientation that can be observed in real-time using polarized light. The response was both sensitive and selective: reorientation was observed at target concentrations on the order of the aptamer disassociation constant, but no response was observed in control experiments with target analogues. Circular dichroism and resonance energy transfer experiments suggested that the LC reorientation was due to a conformational change of the aptamer upon target binding. Specifically, under conditions where aptamer-ligand binding induced a conformational change from a relaxed random coil to more intricate secondary structures (e.g. double helix, G-quadruplex); a transition from planar to homeotropic LC orientation was observed. The mechanistic understanding gained in these studies reveals how subtle changes in hydrophobic adsorbates can induce dramatic changes in the associated interfacial structure. Furthermore, these observations suggest the potential for a label-free LC-based detection system that can simultaneously respond to the presence of both small molecules and nucleic acids.

•*Quantum Liquid Crystals* – We studied a number of physical systems that exhibit quantum liquid-crystalline orders. Namely, in additional to quantum order, such systems exhibit partially broken spatial symmetries. Examples that we have studied and continue to explore include helical and frustrated quantum magnets as well as phases of resonant atomic gases. In the latter class, we have studied s-wave resonant imbalanced Fermi gas and a p-wave resonant Bose gas. In the former, the liquid-crystalline smectic, nematic and rich variety of other descendant states emerge from strongly quantum- and thermally- fluctuating Fulde-Ferrell and Larkin-Ovchinnikov superconducting states, driven by a competition between resonant pairing and Fermi-surface mismatch. In the latter, we found that at intermediate detuning the p-wave resonant interaction generically drives Bose-condensation at a finite momentum, set by a competition between atomic kinetic energy and atom-molecule hybridization. Because of the underlying rotationally-invariant environment of the atomic gas trapped isotropically, the putative striped superfluid is a realization of a quantum superfluid smectic, that can melt into a variety of interesting phases, such as a quantum nematic. We have mapped out the corresponding rich phase diagrams and transitions, as well the low-energy properties of the phases and fractional topological defects generic to striped superfluids and their fluctuation-driven descendants.

*•Spatial Patterning of Disclination Clusters and Their Use for Optical Vortex Generation* – Topological defect lines are ubiquitous and important in a wide variety of fascinating phenomena and theories in the fields ranging from early-universe cosmology to optics, condensed matter and particle physics, topology and category theories in mathematics, and to engineering of materials and beams. For example, optical orbital angular momentum transfer can be enabled by optical vortices, "dark thread" singular lines around which the light's momentum swirls. The state of the art display panels with unprecedented refresh rates and controllable viewing angles16 are nowadays made of a liquid crystal in the so-called "blue phase" that contains a periodic network of defect lines threading the medium. Defects like cosmic strings and vortex lines in electron beams are hard to obtain and study but often can be understood by probing defects in other topologically similar systems, like liquid crystals and light. Graduate student Paul Ackerman has described facile erasable "optical drawing" of self-assembled defect clusters in liquid crystals. These quadrupolar defect clusters, stabilized by medium's chirality and the tendency to form twisted configurations, are shaped into arbitrary 2D patterns, including reconfigurable phase gratings capable of inducing and controlling optical phase singularities in laser beams. The highly-controlled localized structures of defect cluster may be utilized to mediate novel modes of elasticity-mediated interaction and self-assembly of colloidal inclusions of various shapes and material composition in LCs. This work bridges the study of defects in condensed matter physics and optics and may enable new applications in singular optics, display and diffractive devices, data storage, etc. *•Nonlinear*

*Photoluminescence from Graphene Oxide Flakes* - We have reported a visible-range nonlinear photoluminescence (PL) from graphene oxide (GO) flakes excited by near-infrared femtosecond laser light. PL intensity has nonlinear dependence on the laser power implying a multiphoton excitation process and also strongly depends on a linear polarization orientation of excitation light, being at maximum when it is parallel to flakes. We show that PL can be used for a fully three-dimensional label-free imaging of isotropic, nematic and lamellar LC dispersions of GO flakes in water. This nonlinear PL is of interest for applications in direct label-free imaging of composite materials and study of orientational ordering in mesomorphic phases formed by flakes, as well as in biomedical and sensing applications of GO.

***Industrial Outreach***

The Colorado high tech industry community continues to benefit from the Center. Center graduate students and postdocs have taken jobs in several local companies, including the R&D group at RealD, which recently gained recognition for providing the technical underpinnings of the modern 3D movies, including Avatar. A Center graduate (Chair of the Center Technology Advisory Board) is working in Boulder County in the R&D group for Serious Materials, with the goal of improving on their world-class energy efficient windows.

A major development in 2013 was the Center invention of Fisheye Lens Conoscopy, one of the most significant developments in the characterization of the birefringence of materials in the last 150 years. Fisheye Lens Conoscopy will enable real-time monitoring of the thickness of food packaging plastic films during their manufacture.

The Center has been a major innovator in the field of ferroelectric liquid crystals (FLCs) for many years. Displaytech, Inc., a Colorado company founded by the Center PI and Co-PI, has successfully commercialized FLC in the form of microdisplays for camera viewfinders and hand-held picoprojectors. The Displaytech team continues to manufacture liquid crystals for its display products in Longmont.

Center researcher David Walba is currently an Associated Researcher at the National Renewable Energy Laboratory, working on liquid crystal composites for organic photovoltaic (OPV) devices. This project, which developed as a result of a Center sponsored LCOPV workshop, aims to evaluate the electrical and photoresponse characteristics of the Center's helical nanofilament (HNF) phases for organic photovoltaic applications. UCB graduate student Rebecca Callahan

Initial experiments, in which the photogenerated carrier lifetimes in HNF structures doped with C60 homolog PCBM have proven to be exceptionally exciting, with these composites exhibiting extremely long carrier lifetimes.

***Education Outreach***

Highlights from the past year include expansion of the *Materials Science from CU* program, now one of CU's most effective K-12 outreach programs. In outreach to children (and parents), the focused attention of a dedicated outreach Director has enabled many notable successes over the past year. Examples include:

*Materials Science from CU* delivered 110 classes to 4,200 Colorado children, bringing Center personnel into the classroom using the understanding of materials to teach physical science concepts (~2,000 classes to 80,000 students over the past 11 years).

Center senior investigators participated in in a variety of high school and undergraduate research experience and undergraduate/graduate minority access programs in 2013.

The LCMRC NSF Partnership for Research and Education in Materials (PREM) funding for support of undergraduate and graduate research opportunities now has two of its minority undergraduate students pursuing Ph.D.s in the Center.

**CHECRA Report for 2013**

**Engineering Research Center in Extreme Ultraviolet Science and Technology**
**Colorado State University**
**University of Colorado**
**Director:** Prof. Jorge J. Rocca. Colorado State University
**Deputy Director:** Prof. Margaret M. Murnane. University of Colorado
**CHECRA Grant**: $200,000 (2008, 2009), $400,000 (2010-2013)

**Project Summary**
The National Science Foundation (NSF)-funded Extreme Ultraviolet Science and Technology Engineering Research Center, a partnership between Colorado State University and the University of Colorado, is a world leader in the generation and application of light beyond the ultraviolet to challenging scientific and industrial problems that include nanotechnology, advanced materials, clean energy, and in the near future biology. The Center was supported by $1.77 Million from NSF core funding in 2013. The funding provided by the Colorado Higher Education Competitive Research Authority (CHECRA) was crucial in assisting the Center to achieve renewal by the National Science Foundation for 2010-2013. The Center was recently granted an extension until June 30, 2014. The CHECRA support also contributed to the Center's ability to obtaining funding from NSF and other Federal agencies. For example, during 2013 the Center received an additional $0.8 Million grant co-funded by NSF and by one of Center's corporate members, Cymer Inc. During the past year, the Center also received $142 K in industry funding, and a grant from NSF for $0.318 Million to run a Research Experience for Teachers program during the next three years (2014-2017). The Center is thus making important contributions to the research output, education, industrial and economic health of the state.

**Description of the project, the principal persons or entities involved in the project**
Light in the Extreme Ultraviolet (EUV) region of the spectrum (wavelengths approximately 1 to 50 nm) has become a critical enabling technology in areas of great importance to the national economy, as the size of the most advanced electronic circuits and nanoscale machines continues to shrink below the wavelength of visible light. Furthermore, exciting new opportunities in science arise from the possibility of focusing EUV light to unprecedented small spot sizes, short pulse durations, and extremely high intensities. Further development of EUV technologies will open up a variety of new areas of investigation, including new tabletop probes of surface, chemical, cellular samples, nanostructures and materials, and the development of a new generation of nanoprobes. In response to these challenges and opportunities, in October 2003 NSF funded the ERC in Extreme Ultraviolet Science and Technology.

The Center combines the complementary expertise of Colorado State University and the University of Colorado—leaders in compact EUV light sources and applications—with a set of partner institutions that include the University of California Berkeley/Lawrence Berkeley National Laboratory and four year Colleges, other universities, national laboratories, and a set of sixteen industrial corporate members. At Colorado State University Center the faculty includes Profs. Jorge Rocca, Carmen Menoni, Mario Marconi, and Elliot Bernstein with affiliations to the Electrical Engineering, Chemistry, and Physics departments. At the University of Colorado the Center Faculty includes Profs. Margaret Murnane, Henry Kapteyn and Ronguii Yang, with affiliations to the Physics Department, JILA, the Electrical and Computer Engineering and Mechanical Engineering Departments.

To realize the full impact of EUV technology in manufacturing and in scientific research we are developing a new generation of compact coherent EUV sources with unique capabilities and we are combining them with advanced EUV optics to implement engineered systems designed to solve challenging engineering and scientific problems. Breakthroughs in new EUV lasers and in High Harmonic Generation sources have significantly expanded their spectral coverage, in some cases increasing the average power by orders of magnitude. In the past year we have made significant advances in the development of compact high brightness coherent EUV and soft x-ray sources and have broken new ground and established new records in integrating them into engineered systems. By integrating the new compact sources with advanced EUV optics, we have developed a new set of microscopes, materials modification stations, and spectrometers with unique capabilities for a broad range of applications in industry and science. These include compact EUV microscopes with sub-38 nm resolution, a laser ablation testbed capable of producing sub-100 nm holes, an EUV photoacoustic metrology testbed to characterize thin films, a lensless microscope with 20 nm spatial resolution and elemental sensitivity, a single photon ionization spectrometer for the study of nanoclusters, a table-top workstation for the patterning of arrays of nanostructures;

This Center makes an important contribution to education in Colorado, ranging from graduate and undergraduate education to elementary school. We are addressing the shortage of engineers and scientist with expertise in EUV technology by training a large number of students and young scientists, several of which have now graduated and joined industries in Colorado. Our Research Experience for Undergraduate program (summer and year-round) has already mentored more than 200 students, with a significant fraction of the summer participants from under-represented minority groups. During 2013 the Center received $ 0.318 Million of additional funding from NSF to establish and RET site, to provide research experiences for high school and middle school science teachers during 2014-2017. The teachers conduct research at the Center and develop material they can take back to the classroom. During the summer of 2013 we also continued with our NSF funded REU program that provides research experiences to undergraduate students. We supported 28 undergraduate students to conduct research at CSU and CU. We have also developed a successful set of workshops for K-12 students and teachers. The Center also supported High School student researcher interns during the summers. During the summer of 2013, we provided research experiences for 8 high school students. Optics teaching kits containing materials and curriculum for standards-based hands-on activities were distributed to over 100 K-12 teachers. In 2013 we continued to hold the annual "Optics After School" Lab program for High School Students. This 5 day event has enrolled the participation of nearly 200 High School students since the Center started. To further ensure the active participation of under-represented groups, the Center is working with the Office of Diversity at CSU and a collaboration with the SMART program at CU–Boulder.

**The amount of funding allocated to each principal person or entity, manner in which each entity applied the funding in connection with the project, and results achieved**

The $400K in state matching funds to the Center for 2012 were distributed in equal parts among Colorado State University and the University of Colorado to support graduate students and young scientists who worked in collaboration at Colorado State University and at the University of Colorado to develop new sources and applications of EUV laser light

At Colorado State University, the CHECRA matching funds for the NSF EUV ERC are used to support graduate students and a research scientist, who worked in the projects described below . In 2013 part of the Center building was moved into a new laboratory specifically designed for laser research. During 2013 we also continued the development of extreme ultraviolet and soft x-ray lasers for applications in nano-scale imaging, error-free printing of nano-scale patters, and other applications as described in the publications below. We demonstrated for the first time uninterrupted laser operation at a record 100 Hz repetition rate. Lasing of this high repetition rate laser was also extended to shorter wavelengths. Using a novel interferometer we measured the line width of these lasers, an important parameter for applications such as nano-scale holography imaging. Efforts in nano-scale imaging also continued with the first table-top demonstration of recording of a holographic movie that recoded the rapid motion of nan-scale objects. Finally, we continued to make progress in the development of a new type of analytic laser probe that using the superior spatial resolution of focused EUV laser light to map the composition of materials with nano-scale resolution. A depth resolution of 20 nanometers was demonstrated. A collaboration continued with a spin-off company in Fort Collins (XUV Lasers), to commercialize one of the compact EUV laser sources developed at the Center.

The University of Colorado used their $200K State Matching funds for the NSF EUV ERC to support a postdoctoral researcher and two graduate students. These young scientists worked on key technologies of the Center – the development of compact laser and x-ray sources with wavelengths less than 1 nanometer, and also the development of new microscopy and nanometrology techniques. A major advance occurred in 2013, with the demonstration of a bright tabletop x-ray source, as well as a general approach for nanoscale imaging and metrology. These new capabilities are attracting interest from industry. Many applications of these technologies are being implemented in collaboration with NIST Boulder Labs, industry and other collaborators including: the development of new microscopes capable of high-resolution nanoimaging of thick materials samples; characterization of interfaces and thin films of interest to the semiconductor and data storage industries; measurements of heat transport in nanostructures of interest to electronics and photovoltaics; and understanding and optimizing magnetic materials on nanoscale dimensions for applications in data storage. [see references] Past work on laser and x-ray sources has already been commercialized and has led to a 38-person spin-off company in Boulder. [KMLabs link:**www.kmlabs.com.**] The current work on new coherent x-ray sources and advanced microscopes will also be commercialized in the future.

**Summary to Benefits to the State of Colorado**

- In 2013 the Center received $1.777,000 for core funding from the NSF.
- On top of this NSF core funding , the Center generated $ 3.8 M in funding from Federal Agencies during 2013 for Colorado State University and University of Colorado.
- The Attracted $142,000 in funding from industry during 2012, of which $100,000 were in cash
- Supported ~ 75 graduate and undergraduate students and faculty in Colorado
- Graduated numerous students with PhD or MS degrees who were hired by Colorado high
- technology companies.

- Assisted Colorado companies in bringing new products to the market (e.g., KM laboratories, XUV Lasers)
- Provides research experiences for undergraduate students ( 28 students at CSU and CU during 2013)
- Reached 310 K-12 students and 25 teachers with science workshops and
- demonstrations during, 2013.
- Continued to provided summer research experiences for middle school teachers and high school teachers, 4 during 2013
- Research experiences for high school students ( 8 high school students during 2013).
- Increases the National and International reputation of Colorado as a leader in advanced technology and science.

**Center Peer Review Journal Publications for 2013**


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22. B. Bernhardt, A. R. Beck, X. Li, E. R. Warrick, M. J. Bell, D. J. Haxton, C. W. McCurdy, D. M. Neumark, and S. R. Leone, "High-spectral-resolution attosecond absorption spectroscopy of autoionization in xenon," Phys. Rev. A 89, 023408 (2014).
23. M.-F. Lin, D. M. Neumark, O. Gessner, and S. R. Leone, "Ionization and dissociation dynamics of vinyl bromide probed by femtosecond extreme ultraviolet transient absorption spectroscopy," J. Chem. Phys. (in press) (2014).
24. B. A. Reagan, W. Li, L. Urbanski, K. A. Wernsing, C. Salsbury, C. Baumgarten, M. C. Marconi, C. S. Menoni, and J. J. Rocca, "Hour-long continuous operation of a tabletop soft x-ray laser at 50-100 Hz repetition rate," Opt. Express 21, 28380-28386 (2013).
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**Engineering Research Center Reinvention of the Nation's Urban Water Infrastructure (ReNUWIt)**
**Colorado School of Mines**
CHECRA Grant: $400,000 (per year for 5 years)
Reporting Period: January 1-December 31, 2013

**Summary:** The Engineering Research Center (ERC) for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt) at the Colorado School of Mines, under the leadership of Dr. John E. McCray, is a collaborative effort among four research universities in the West, CSM, Stanford University, University of California at Berkeley, and New Mexico State University. The ERC was established on August 1, 2011 and is the first center to focus on civil infrastructure ever funded by the National Science Foundation.

Cities are facing a mounting water crisis from climate change, population expansion, ecosystem demands and deteriorating infrastructure that threatens economic development, social welfare, and environmental sustainability. Without relatively large investments this crisis will only deepen through the 21st century. Accordingly, the goal of this ERC is to advance new strategies for water/wastewater treatment and distribution that will eliminate the need for imported water, recover resources from wastewater, and generate rather than consume energy in the operation of urban water infrastructure while simultaneously enhancing urban aquatic ecosystems. While many existing approaches could be used to transition urban water infrastructure to this more sustainable state, their implementation currently is limited by uncertainties about their long-term performance, life cycle costs, institutional impediments and public concerns about unfamiliar technologies.

**Description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity**

To meet the challenges described above, ReNUWIt has launched key research projects within three research thrust areas. These research thrust are defined as follows:
(1) **Efficient Engineered Water Systems:** Decrease reliance on inefficient centralized treatment systems by employing distributed treatment systems that embrace water conservation, local use of alternative supplies, energy management, nutrient recovery, and that integrate with existing infrastructure;
(2) **Natural Water Infrastructure Systems:** Integrate managed natural systems into water infrastructure to fully realize the potential benefits that natural systems can provide with respect to water storage and improvement of water quality, while simultaneously rehabilitating urban hydrology and aquatic habitat;
(3) **Urban Systems Integration and Institutions:** Support the reinvention and restoration of urban water systems through the development of decision-making tools that account for economic, environmental and social factors and development of approaches that can circumvent impediments to change posed by regulations, laws, jurisdictional fragmentation, financing and public perception.

Water resource planners are hesitant to integrate new types of engineered treatment systems into their water portfolio due to uncertainties about cost, reliability, public health risks, and overall impacts on system performance. Thus, a mechanism for technology assessment is needed at scales ranging from the laboratory to the full-scale service area. Such capabilities do not exist in the public, private, or academic sectors, and as a result, many good ideas are not brought into practice. To facilitate the integration of new technologies into urban water systems, tools like life-cycle assessment for decision-making are being advanced and research on engineered systems that support the concept of tailored water for distributed non-potable and potable water reuse, energy-positive wastewater treatment and nutrient recovery, concentrate management, and enhanced water recovery is being conducted.

The goal of the *Efficient Engineered Systems* research thrust is to characterize the viability of existing but underutilized technologies at different scales by assessing their economic, environmental, and social costs and benefits. The specific aims of this thrust are: (i) to identify the most efficient scale of implementing more sustainable engineered water systems; (ii) to provide new, resilient technologies leading to energy-positive wastewater treatment and recovery of nutrients; (iii) to develop technologies that provide water tailored to meet specific needs including alternative water delivery systems; and, (iv) to develop energy-efficient hybrid systems for concentrate management and enhanced water recovery.

At CSM, the *Efficient Engineered Systems* research thrust is supported by two research groups (E1 and E2). Research group E1 develops engineered solution to facilitate reuse of municipal wastewater effluent tailored to local needs. The engineered solutions will be part of a smart urban water grid where distributed treatment systems facilitate water reuse while minimizing the overall energy and carbon footprint. These approaches require the design and operation of highly flexible treatment systems that are remotely monitored and supervised. A high degree of flexibility is needed since water reuse needs can change as a function of season and location. Treatment systems developed and tested under E1 are using hybrid technologies using sequencing batch reactors coupled with membrane bioreactor processes. S elective desalination processes, such as electrodialysis reversal, are employed to remove certain salts that limit certain reuse applications. In addition, research group E2 will focus on treatment processes that enable the recover of energy contained in wastewater streams through modified anaerobic processes and use of microalgae. These efforts are supported through close collaborations with industry partners and start-up companies in Colorado.

Throughout the 19th and 20th centuries, natural aquatic systems had an uneasy coexistence with water infrastructure. As urban population increased, engineered structures replaced natural aquatic systems as surface waters were routed to storm sewers and urban hydrology was altered by impermeable surfaces reducing groundwater infiltration. During the latter half of the 20th century, recognition of the adverse impacts on aquatic systems from the discharge of wastes and modification of urban hydrology led to the passage of the Clean Water Act and Federal Bonds to support the construction of treatment systems to protect aquatic ecosystems. While this approach resulted in dramatic improvements in water quality, water managers are increasingly cognizant of its limitations and have begun to advocate for the integration of natural systems into urban water infrastructure as a means of enhancing water quality, improving system resiliency, and reducing energy consumption while simultaneously preserving ecosystem integrity and providing aesthetic benefits. Unfortunately, natural systems are complex, and our understanding about how to actively manage them as part of urban water infrastructure is limited. As a result, water managers are uncertain about how to invest in projects involving managed natural systems. Furthermore, our failure to understand how natural systems respond to active management prevents us from fully realizing the potential benefits they can provide with respect to water storage and the improvement of water quality.

The thrust area on the use of natural water infrastructure systems will bring a much-needed quantitative approach to an area that has not previously been subjected to rigorous engineering analysis. Research at CSM will employ advances in fundamental understanding of natural systems to remove impediments to integrating natural systems into water infrastructure by making the complex processes that affect water transport, quality and ecosystem function in natural systems predictable and manageable. The research is led by three research groups with the goals to: (i) develop tools for manipulating natural systems to enhance water quality (N1); (ii) integrate managed aquifer recharge into urban settings using reclaimed water leading to drinking water augmentation (N3); and (iv) harvest stormwater and infiltrate in urban settings to augment local supplies (N4).

Within the Urban Systems Integration and Institutions thrust, research group U1 focuses on the development of integrated regional water models. These models will serve as decision-support tools for water resource and urban planners and managers to test the performance of treatment and supply options developed in the Natural and Engineered Systems thrusts.

Within the ReNUWIt framework described above, twelve projects were funded in 2013:

- Integrated Regional Economic-Hydraulic Models (U1.1);
- Tools to support decision making for nested, spatially-scaled, integrated urban water infrastructure (U1.2);
- Tailored water for distributed non-potable reuse using sequencing batch/membrane bioreactor hybrid systems (E1.1);
- Sustainable landscape irrigation with reclaimed water (E1.3);
- Point-of-entry water treatment for potable reuse (E1.4);
- Microalgae for wastewater treatment and recovery: A new approach to onsite wastewater treatment (E2.2);
- Anaerobic digestion as primary treatment at WWTPs (E2.4);
- Design of unit process wetlands to optimize chemical contaminant removal (N1.2);
- Hyporheic zone management for water quality improvement (N2.3);
- Managed aquifer recharge and recovery: Simulation, modeling and operation (N3.1);
- Aquifer storage, treatment, and harvesting of stormwater for distributed reuse: coupled modeling, laboratory and field studies (N4.1); and
- Methodologies, models, and materials for predictable removal of chemicals from stormwater during distributed recharge (N4.3).

| Principal Investigators | Funding from CHECRA |
|---|---|
| John McCray, CSM Principal Investigator | |
| Center Lead | $129,827 |
| Project Lead, Hyphorheic Management, N2.3 | $13,690 |
| Tzahi Cath, Engineered System Thrust Leader | |
| Project Lead, Decision Support Tools, U1.2 | $21,722 |
| Project Co-Lead, Tailored Water, E1.1 | $25,601 |
| Project Lead, Microalgae Wastewater Treatment, E2.2 | $1,174 |
| Jörg E. Drewes | |
| Project Co-Lead, Tailored Water, E1.1 | $25,601 |
| Project Lead, Point-of-Entry Treatment, E1.4 | $34,669 |
| Project Co-Lead, Unit Process Recharge, N3.2 | $2,749 |
| Linda Figueroa | |
| Project Lead, Anaerobic Digestion, E2.4 | $7,827 |
| Christopher Higgins | |
| Project Lead, Subsurface Purification, N4.3 | $23,046 |

| | |
|---|---|
| Reed Maxwell<br>Project Lead, Managing Complex Urban Water, U1.1<br>Project Lead, Coupled Modeling, N4.1 | <br>$80,592<br>$61,164 |
| Barbara Moskal, Education Lead<br>(funds in 2013 were from NSF and CSM) | <br>$0 |
| Junko Munakata-Marr<br>Project Lead, Sustainable Irrigation, E1.3 | <br>$29,305 |
| Jonathan Sharp<br>Project Lead, Unit Process Wetland, N1.2<br>Project Co-Lead, Unit Process Recharge, N3.2 | <br>$9,651<br>$2,749 |
| Kathleen Smits<br>Project Lead, Aquifer Management, N3.1 | <br>$21,286 |
| ***TOTAL SPENDING (Jan-Dec 2013)***<br>*(includes carryover funds from 2012)* | <br>***$490,652*** |

**The manner in which each principal person or entity applied the funding in connection with the project**

John McCray: Discretionary Center funding for supporting new research directions; design and installation of new testing apparatus; travel support for students and faculty; and partial support of a post doc to oversee operations at the Mines Park Test Site. One graduate student is studying water quality improvements in the hyporheic zone to develop management strategies for urban stream restoration (N2.3). Tuition and stipend support for this student is from an NSF Scholarship. CHECRA Funding supported one non-thesis graduate student and an undergraduate hourly research student (N2.3). Nominal funding was also used for materials and supplies for construction of field testing apparatus (N2.3).

Tzahi Cath: Partial salary support for an Assistant Research Faculty member to develop a decision support tool to aid tailoring water treatment for specific beneficial use (U1.2). Funding for one graduate student focused on energy optimization and tailored non-potable reuse (E1.1). Partial salary support for one postdoctoral research associate to manage the full-scale sequencing batch reactor with submerged ultrafiltration membrane bioreactor (SBMBR) and nominal funding was also used for materials and supplies for SBMBR operation (E1.1). Nominal funding used to cover an hourly undergraduate student for bench scale testing of nutrient and energy recovery from wastewater using specific target microalgae (E2.2).

Jörg E. Drewes: Funding for one graduate student who is developing a prototype using ceramic nanofiltration membrane coupled with UV oxidation for point-of-entry drinking water treatment (E1.4). Nominal funding was also used for materials and supplies for SBMBR operation (E1.1). Note NSF funds supported one additional graduate student (E1.1).

Linda Figueroa: Tuition support for a graduate student who is developing a pilot-scale reactor for methane recovery in cooperation with Plum Creek Wastewater Authority, Castle Rock, CO (E2.4).

Christopher Higgins: Partial funding for one graduate student who is developing special adsorbants to remove chemical contaminants in stormwater during distributed recharge (N4.3). The remaining support for the graduate student was from a NSF Scholarship. Partial support for a post doc for life cycle cost assessment. Funding also provided for materials and supplies in support of chemical analysis using liquid chromatography tandem mass spectrometry (LC-MS/MS).

Reed Maxwell: Salary support for one postdoctoral research associate and one graduate student who spearheaded initial hydrological modeling efforts for modeling case study in close collaboration with Aurora Water, CO (U1.1). Funding for a second postdoctoral research associate who develops watershed-scale models to locate distributed stormwater recharge facilities (N4.1). This study is currently focusing on the Cherry Creek water shed in Denver.

Junko Munakata-Marr: Funding for one graduate student and one hourly undergraduate graduate student for the establishment of test cells for soil treatment of irrigated reclaimed water (E1.3). Nominal funding for materials and supplies needed for monitoring of the test cells. Supplemental NSF funding also supported an undergraduate student via a Vetreran Research Supplement, a nontraditional REU student to conduct sampling, and a Brazilian exchange student to assist with sampling, analysis and preparation of education materials.

Jonathan Sharp: Funding to cover supplies and materials to study the biocommunity diversity in unit processes wetlands to better understand key boundary conditions for the attenuation of trace organic chemicals (N1.2). Note NSF funds supported one graduate student (N1.2). Supplemental NSF funding also sponsored a REU student to develop and monitor POP flow through cells linked to Mines Park MBR and a Native Americal REU student to look at molecular / microscopy tools for understanding microbial biofilms.

Kathleen Smits: Funding for one graduate student who designed and constructed a 3-D intermediate-scale tank experiment to simulate fate and transport processes of artificial recharge and recovery facilities (N3.1).

**Results Achieved**

Center scientists and engineers have established a research test bed on the Colorado School of Mines campus that utilizes and treats municipal wastewater (~7,000 gal/day) in a demonstration-scale treatment unit to tailor effluent qualities to various reuse applications (i.e., urban landscape irrigation; toilet flushing; streamflow augmentation; groundwater recharge) (E1). This effort continues to be supported through collaborations with manufacturers and start-up companies within Colorado. Strategies for optimization of generating on-demand effluent qualities with elevated levels of nitrogen while simultaneously optimizing energy demands continue to be established (E1). A second season of irrigation was begun with collection and analyses of leachate and soil samples to assess using tailored water for irrigation to reduce potable use, reduce the application of mineral fertilizers, and minimize nitrate leaching to groundwater. Energy recovery via gasification of algae and algae waste and anaerobic primary treatment, in addition to thermochemical extraction of energy from wastewater biosolids, are being explored (E2).

Activities within the natural water infrastructure systems thrust included the upscaling of testing at the field scale. In N.3, CSM investigators helped to design anopen water wetlands cell constructed at Prado by the Orange County Water Department, and installed a new testbed to install water treatment features in streambeds for treating storm-water pollutants and promote cleaner water leaving our cities. These modules were termed "Biohydrochemical Stream Water Treatment (BEST)" modules and an invention disclosure has been filed at CSM. In N.3, researchers are working with Aurora Water to develop smarter, more efficient methods for infiltrating recycled water for aquifer storage while simultaneously improving water quality. The technology is termed SMART (smart managed aquifer recharge technology). In N.4, new geomedia is being researched for it's potential reo remove stormwater pollutants during infiltration in engineered low-impact development (LID features). In addition, a high-resolution spatial model was developed for the south Denver area to simulate the many interacting effects of storm water and water supply including the potential impacts of new water infrastructure.

Center scientists within the U1 research group have developed a conceptual model that couples supply options with demand while also considering water treatment/distribution as well as wastewater collection and treatment. This model will be tailored to serve as regional model for major water utilities, such as Aurora Water, to investigate how utilities might deploy technologies, strategies, and policies in order to increase overall efficiency of water and energy use. The model will also allow characterizing inefficiencies in the current system. The model is based on a flexible, module-based simulation framework.

**Summary of Benefits to the State of Colorado**

- Received $805,000 NSF core funds in 2013. These funds in combination with CHECRA funds and $313,189 CSM matching funds supported 14 PhD and masters graduate students, 5 undergraduate students, 10 faculty, 4 post-doctorial fellows, 2 assistant research professors, and 3 research staff.
- Bi-monthly seminars organized and sponsored by the ReNUWIt students. Seminar speakers and topics include a range of student research, industry partners, and experts.
- Hosted a workshop at the 2013 Association of Environmental Enginerering and Science Professors (AEESP) Research and Education Conference held at CSM in July 2013.
- Gave a tour of turfgrass test bed (E1.3) to about 50 visitors from Annual WateReuse Symposium, representing industry, government and academia.
- Delivered two days of water-related workshops to K-6 teachers from Adams County.
- Developed and staffed hands-on water quality booths (microscopy and Enviroscape) for Mitchell Elementary Math and Science Night. Also provided classroom time for 2nd graders during delivery of Environmental Learning for the Future models at Mitchell Elementary.
- Developed and delivered modules and lesson plans on Water Quality and Water Impurities for Bechtel Teaching Earth, Energy and Environment in Elementary Mathematics and Science Teachers
- Held the Summer Teacher Institute workshop highlighting water with 10 elementary and middle school teachers from Colorado participating.
- Delivered Dyslexic Camp for 32 dyslexic students (grades K-7) providing the opportunity to experience success in science.

**Publications and Presentations in 2013 (funded wholly or in part with CHECRA funds):**

**<u>Thesis and Dissertations:</u>**

Roux, V. 2013. Leachate Quality and Denitrifying Gene Abundance During Establishment of Turfgrass Irrigated with Tailored Membrane Bioreactor Effluent. M.S. Thesis, Civil and Environmental Engineering, Colorado School of Mines.

**<u>Publications:</u>**

Bischel, H.N., J.E. Lawrence, B.J. Halaburka, M.H. Plumlee, A.S. Bawazir, J.P. King, J.E.

McCray, V.H. Resh, R.G. Luthy. 2013. Renewing urban streams with recycled water for streamflow augmentation: Hydrologic, water quality, and ecosystem services management. *Environmental Engineering Sci.*, 30(8), 455-479.

Condon, L.E. and Maxwell, R.M. 2013. Implementation of a linear optimization water allocation algorithm into a fully integrated physical hydrology model. *Advances in Water Resources*, 60, 135-147, 2013.

Condon, L.E. and Maxwell, R.M. Groundwater-fed irrigation impacts spatially distributed temporal scaling behavior of the natural system: A spatio-temporal framework for understanding water management impacts. *Environmental Research Letters*. In press.

Condon, L.E. and Maxwell, R.M. Feedbacks between the managed and natural system: Diagnosis of temporal and spatial patterns in an irrigated basin using an integrated hydrologic model. *Water Resources Research*. In Review.

Homme C. and Sharp J.O. 2013. Differential microbial transformation of nitrosamines by an inducible propane monooxygenase. *Environ Sci Technol.* 47(13): 7388-95.

Jasper J.T., Nguyen M.T., Jones Z.L., Ismail N.S., Sedlak D.L., Sharp J.O., Luthy R.G., Horne A.J., Nelson K.L. 2013. Unit process wetlands for removal of trace organic contaminants and pathogens from municipal wastewater effluent. *Environ Eng. Science*. 30(8): 409-420.

Lawrence, J.E., Skold, M.E., Hussain, F.A., Silverman, D.R., Resh, V.H., Sedlak, D.L., Luthy, R.G., McCray, J.E. 2013. Hyporheic zone management in urban streams: A review and opportunities for enhancing water quality and improving aquatic habitat by active management, *Environmental Engineering Sci.*, 30(8), 480-501.

Li D., Alidina M., Ouf M., Sharp J.O., Saikaly P., Drewes J. 2013. Microbial community evolution during managed aquifer recharge in response to different biodegradable dissolved organic carbon (BDOC) concentrations. *Water Research* 47: 2421-2430.

Li D., Sharp J.O., Saikaly P., Ali S., Alidina M., Alarawi M.S., Keller S., Hoppe-Jones C., Drewes J. 2012. Dissolved organic carbon influences microbial community composition and diversity in geographically distinct managed aquifer recharge systems. *Appl. Envron. Microbiol. 78(19):6819.*

Lopez S.R., Hogue T.S., and Stein. E.D. 2013. A framework for evaluating regional hydrologic sensitivity to climate change using archetypal watershed modeling. *Hydrology and Earth System Sciences*, DOI:10.5194/hess-17-3077-2013.

Lopez S.R., Maxwell R.M. 2013. Extracting urban features from LiDAR using GIS and spatial filtering techniques, *Remote Sensing*, In Preparation.

Lopez S.R., Maxwell R.M. 2013. Advancing urban stormwater modeling: Ultra-high-resolution evaluation of best management practices, *Environmental Research Letters*, In Preparation.

Lumley, N.P., Braun, R.J., Cath, T.Y., Prieto, A.L., Ramey, D.F., Porter J.M., Techno-economic analysis of wastewater sludge gasification: A decentralized urban perspective, *Bioresource Technology* Submitted 2013, in review.

Ramey, D.F., Lumley, N.P., Prieto, A.L., Porter J.M., Cath, T.Y. Evaluating air blown gasification for energy recovery from wastewater solids: Impact of biological treatment and point of generation on energy recovery, *Environmental Science and Technology*, Submitted 2013 in review.

Regnery J., Lee J., Kitandidis P., Illangasekare T., Sharp J.O., Drewes J. 2013. Integration of managed aquifer recharge systems in urban water infrastructure – overcoming current

limitations and engineering challenges. *Environ Eng. Science*. 30(8): 421-436.

**Presentations:**

Beardsley S., Jones Z., Sharp J.O., and Sedlak D.L. 2013. Biotransformation of trace organic contaminants in vegetated treatment wetlands. *8th Micropol & Ecohazards Conference*, Zurich, CH. June 17-19, 2013.

Condon, L.E. and Maxwell, R.M. 2013. Using integrated modeling to understand feedbacks between groundwater-surface water interactions and water management decision making, Poster for *MODFLOW and More*, Golden, CO, Jun 2-5, 2013 *Outstanding student poster award

Condon, L.E., Maxwell, RM, Condon, L. 2013. Using integrated modeling to understand feedbacks between groundwater-surface water interactions and water management decision making, Poster for *Association of Environmental Engineering and Science Professors (AEESP) 50th Anniversary Conference*, Golden, CO. July 14-16, 2013.

Condon, L.E. and Maxwell, R.M. 2013. Why groundwater matters: An innovative look at pumping, irrigation, system dynamics and sustainability, Presentation for *Geological Society of America*, Denver, CO, Oct 27-30, 2013.

Condon, L.E. and Maxwell, R.M. Why groundwater matters: An innovative look at pumping, irrigation, system dynamics and sustainability, Poster for *American Geophysical Union*, San Francisco, CA, Dec 9-13, 2013.

Homme C. and Sharp J.O. 2013. Differential nitrosamine biotransformation by a bacterial propane monooxygenase. Poster for *113th General Meeting American Society for Microbiology*, Denver, CO. May 18-21, 2013.

Jones Z.L., Jasper J., Beardsley S., Sedlak D., Sharp J. 2013. Unit process wetlands: Microbial ecology and function. Poster for *Conference on Earth and Energy Research (CEER)*, Golden, CO. Feb 21-22, 2013

Jones Z.J., Jasper J., Beardsley S., Sedlak D., Sharp J. 2013. Wetlands for the attenuation of trace organic contaminants. Poster for *RMSAWWA*, Golden, CO. May 14, 2013.

Jones Z.J., Jasper J., Beardsley S., Horne A., Sedlak D., Sharp J. 2013. Unit process wetlands: The attenuation of trace organic contaminants. Poster for *AEESP 50th Anniversary Conference*, Golden, CO. July 14-16, 2013.

Jones Z.L., Jasper J., Beardsley S., Sedlak D., Sharp J. 2013. Open water wetland cells as a part of a unit process wetland. Presentation for *Consortium for Research and Education on Emerging Contaminants (CREEC)*, Denver, CO. December 12, 2013.

Li D., Alidina M., Sharp J.O., Drewes J.E. 2013. Microbial community characteristics in managed aquifer recharge systems and relationship with trace organic compounds removal. Presentation for *IWA Microbial Ecology and Water Engineering*, Ann Arbor, MI. July 7-10, 2013.

Li D., Sharp J.O., Drewes J.E. 2013. Microbial community characteristics in managed aquifer recharge systems and relationship with trace organic compounds removal. Presentation f for *AEESP 50th Anniversary Conference*, Golden, CO. July 14-16, 2013.

Li D., Alidina M., Drewes J.E., Sharp J.O. 2013. Microbial community structure and function in saturated riverbed and laboratory sediments. Poster for *113th General Meeting American Society for Microbiology*, Denver, CO. May 18-21, 2013.

Lopez S.R. and Maxwell R.M. 2013. Urban Stormwater Modeling: Ultra-high-resolution evaluation of best management practices, Presentation for *American Geophysical Union*, San Francisco, CA, Dec 9-13, 2013.

Lopez S.R., Maxwell R.M., Condon L. 2013. Ultra-high-resolution hydrologic modeling of stormwater routing and infiltration in an urban watershed with implementation of best management practices, Presentation for *AEESP 50$^{th}$ Anniversary Conference*, Golden, CO. July 14-16, 2013.

Lopez S.R., Condon L.E., Maxwell R.M. 2013. High resolution hydrologic modeling to investigate urbanization impacts. Poster for Modflow and More, Golden, CO, 2-5 June, 2013.

Appendix E: Colorado State University, CMMAP

## Center for Mulitscale Modeling of Atmospheric Processes (CMMAP)

**Colorado State University**
**Principal Investigators:**
**Center Director:** David A. Randall, Colorado State University
**Deputy Director:** Chin-Hoh Moeng, The National Center for Atmospheric Research, Boulder, Colorado
**Director for Education and Diversity:** A. Scott Denning, Colorado State University
**Director for Knowledge Transfer:** Steve Krueger, University of Utah
**Director for Cyberinfrastructure:** John Helly, University of California, San Diego

## Project Description

The Center for Multiscale Modeling of Atmospheric Processes (CMMAP) is one of seventeen current Science and Technology Centers (STCs) sponsored by the National Science Foundation. Up to this time, CMMAP is the only STC ever awarded in the state of Colorado. CMMAP is a partnership of research and educational institutions, government agencies, and industry.

CMMAP's activities are divided into three areas: (1) research, which is focused on developing a new kind of global atmospheric model; (2) education, outreach and diversity, which seeks to educate and train a diverse population (specifically women, underrepresented minorities, and individuals with disabilities) in climate and Earth System Science; and (3) knowledge transfer, through the sharing of information with other modeling centers and the Colorado Governor's Energy Office. CHECRA funding is being used to support all three of these focus areas.

The Center's research is focused on improving the representation of cloud processes in climate models. Cloud processes are central to the Earth Sciences. Changes in cloudiness can either amplify or damp climate change. In addition, cloudiness and precipitation are key elements of any weather forecast. Clouds are central components of the water cycle. Chemical transformations occur inside clouds and feed back to affect the properties of the clouds. Last but not least, the biosphere is highly dependent on cloud processes. Progress in all of these disciplines is being held back by our limited ability to understand and simulate global cloudiness.

CMMAP's vision is to take advantage of rapidly increasing computer speed to achieve major advances in our ability to understand and predict the effects of clouds on weather and climate, through a revolutionary new approach called the "multi-scale modeling framework" (MMF), in which high-resolution cloud models are coupled to lower-resolution global models. CMMAP's research team includes climate modelers, cloud modelers, and experts on turbulence, radiation, cloud physics, and observations.

CMMAP also has major activities in the areas of Education and Diversity. CMMAP's graduate students are immersed in the Center's culture. They see, and some of them participate in, the training of high-school science teachers and the teaching and mentoring of diverse undergraduates. The students work collaboratively with faculty, solving problems together.

Through "the Center experience," these future leaders are gaining a broad and deep perspective on what it means to be a scientist. In years to come, the larger U.S. society will benefit from this.

The Center's research, education, and diversity missions have the potential to feedback positively on each other. Through its outreach and education work, CMMAP has built credibility with diverse communities. This credibility invites those communities to consider how CMMAP's science mission can serve their priorities. CMMAP's experience in knowledge transfer provides strategies for moving from the basic research to practical knowledge that the communities can use. Finally, the broad experiences of CMMAP graduate students prepare them to link research, education, and diversity. This a positive feedback loop that enriches the research, attracts diverse communities and students, and transfers knowledge to users, all based on the connections that are forged within the Center.

## How the CHECRA funding was used

CHECRA is providing CMMAP with $150,000 per year, total of five years, for a total of $750,000. CMMAP will use the full $150,000 of CHECRA funds allocated for the current year.

The CHECRA funds are partially supporting three administrative professionals and three research scientists at Colorado State University. The administrative personnel are Marcia Donnelson, Connie Hale, and Rodger Ames. They provide essential operational support for CMMAP, including financial management and the organization of a broad range of research, educational, and knowledge-transfer activities. The three research scientists who are receiving partial salary support from CHECRA are Ross Heikes, Celal Konor, and Minoru Chikira. They are developing new mathematical methods to represent weather and climate processes, and doing theoretical work on the role of water vapor in the tropical atmosphere.

In addition, some of the CHECRA funds are being used to support CMMAP's educational work through a subaward to a local non-profit company called Reach. The mission of Reach is to enhance public understanding of science as it relates to our changing world. CMMAP scientists ensure that the materials and curriculum are scientifically accurate, societally relevant and effectively communicated.

## Summary of Benefits to the State of Colorado

- CMMAP was renewed by the National Science Foundation through July 2016, through an award of $17,991,000 to Colorado State University, much of which is used to pay the salaries of staff and graduate students who live in Colorado.
- CMMAP reached over 20,000 K-12 students and teachers through the activities of the Little Shop of Physics (LSOP) in more than 40 school visits, science workshops and the LSOP annual open house.
- CMMAP provided intensive week long training to 45 high school and middle school teachers with the Teaching Weather and Climate Summer Teacher Course.
- CMMAP supported the Windows to the Universe website, which had 6,158,872 page views from 4,050,930 visitors.

Appendix E: Colorado State University, CMMAP

- CMMAP supported 17 CSU graduate students and 12 undergraduate summer interns. Several of these interns are expected to attend graduate school at CSU.
- CMMAP has hosted team meetings in Fort Collins annually bringing about 40 visitors per year to Colorado.
- CMMAP hosted and provided content for two webinars associated with the National Science Teachers Association. The webinars were attended by about 75 science teachers from Colorado and throughout the United States;
- CMMAP hosted the Colorado Global Climate Change Conference at Colorado State University, which was attended by over 350 high school students and 20 high school science teachers.

## Journal Publications for 2013

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3. Arnold, N., M. Branson, M. A. Burt, D. S. Abbot, Z. Kuang, D. A. Randall, and E. Tziperman, 2014: Significant consequences of explicit representation of atmospheric convection at high $CO_2$ concentration. Submitted to *Proc. Nat. Acad. Sci.*
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## Appendix F: School of Mines, Water Quality and Supply Impacts from Climate-Induced Insect Tree Mortality

Integrated GroundWater Modeling Center (IGWMC)
Colorado School of Mines
CHECRA Grant: $75,000 (per year for 5 years)
Reporting Period: January 1-December 31, 2013

Summary: IGWMC received $2.3 million from the National Science Foundation to examine the impact of the pine beetle devastation on vital watersheds in the Rocky Mountain west. The project is led by the Colorado School of Mines in collaboration with research partners from Colorado State University. The study examines the potential water resource changes resulting from the mountain pine beetle epidemic by examining changes in climate, forested ecosystems altered by pine beetle impacts, biogeochemical processes and resource management practices.

(a) A description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity;

Mountain headwaters in the western United States provide drinking water for more than 60 million people, as well as a broad range of agricultural, ecological, tourism, and industrial water users. The Platte and Colorado River basins alone provide water to more than 30 million residential users and 1.8 million acres of irrigated agriculture. A warming trend in the region has been accompanied by unprecedented tree mortality associated with the ongoing mountain pine beetle (MPB) epidemic, and the ramifications of this event on our water resources are not well understood. The goal of our proposed work is to determine potential water resource changes resulting from the MPB epidemic by defining feedbacks between climate change, insect driven forest disturbance, biogeochemical processes and management practices. This is accomplished with laboratory and field studies that feed fully-coupled, regional hydrologic and climatic models to interpret observations and assess management options that are developed through engaging stakeholders.

In addition to directly affecting the hydrologic cycle, climate change increases ecosystem susceptibility to stressors. Warmer winter minimum temperatures and persistent drought conditions have contributed to the ongoing MPB epidemic in the Rocky Mountains that has affected an estimated 4 million acres of lodgepole pine forests. Subsequent insect-induced stressors, such as the emerging engraver and twig beetle populations threatening young trees, are evidence of the long-term nature of this issue. Large-scale forest disturbances due to beetle-killed forests, as well as forest management practices, can significantly alter watershed hydrology, including evapotranspiration, infiltration, runoff, and surface energy fluxes in a region where snowpack is a critical water storage component. We address these land cover perturbations to the hydrologic cycle across a range of scales (hillslope, watershed and regional) using a combination of integrated hydrologic models, hydrologic-atmospheric models and observations.

Just as importantly, soil-vegetation disturbances from beetle-killed forests or forest management may also impact water quality by increasing particulate transport through erosion, increasing nitrification rates and organic carbon fluxes, which can cause decreased soil solution pH, and increasing mobilization and subsequent leaching of metals and metalloids. Similarly, increases in dissolved organic carbon (DOC) in the water supply may lead to increased formation of drinking water disinfection byproducts such as U.S. EPA regulated compounds trihalomethanes, haloacetic acids, and nitrosamines. These potential impacts of climate change, beetle-killed forests, and management practices on water quantity and quality pose significant threats to public health and the regional economy. In order to accurately assess anthropogenic impacts on hydrology and water resources in mountain watersheds an integrated approach must be taken that accounts for interactions and feedbacks not just within the hydrologic cycle but also between the natural (climate, hydrologic, ecological, and biogeochemical) and human (water and forest management) factors that influence water quantity and quality. To directly address the impacts of changing land cover on the fate and transport of metal and organic compounds we employ field and laboratory studies and reactive transport simulations.

| Principal Investigators | Funding from CHECRA |
|---|---|
| Reed Maxwell, Director and Project Lead for Coupled Modeling | $17,765 |
| Jonathan Sharp | $0 |
| John McCray | $0 |
| Alexis Navarre-Sitchler | $5,643 |
| Total Spending (Jan. – Dec. 2013) | $23, 408 |

Students and Postdocs (*funded through CHECRA)

| Name | Affiliation | Work |
|---|---|---|
| Nick Engdahl | CSM postdoctoral research fellow | Multi-scale modeling of the effects of landscape and climate changes on integrated hydrologic systems |
| Colin Penn* | CSM graduate student | Modeling work to incorporate distributed MPB specific parameters into the vegetation aspects of Common Land Model (CLM) |
| Jennifer Jefferson* | CSM graduate student | Modeling an idealized domain with homogeneous forest land cover and a heterogeneous subsurface representation of a Rocky Mountain watershed |
| Moira Pryhoda | CSM graduate student | Pine needle leachate chemistry from a mountain pine beetle infested watershed in Summit County, CO |
| Kristin Mikkelson | CSM graduate student | Bark beetle infestation impacts on nutrient cycling, water quality and interdependent hydrological effects |
| Lindsay Bearup | CSM graduate student | Hydrological effects of forest transpiration loss in bark beetle-impacted watersheds |
| Sophia Seo | CSM graduate student | Sensitivity analysis on the land surface model parameters |
| Brent Brouillard | CSM graduate student | Drinking water quality impacts |
| Nicole Bogenschuetz | CSM undergraduate student | Field characterization of soil mineralization |
| Andrew Maloney | CSU undergraduate student | Stakeholder outreach and surveys |
| Adam Mitchell | CSU undergraduate student | Stakeholder outreach and surveys |

(b) The manner in which each principal person or entity applied the funding in connection with the project

Reed Maxwell: Partial tuition and stipend support for two graduate students at CSM: Colin Penn (MS student, HSE) and Jennifer Jefferson (PhD Student, HSE). Colin is conducting high-performance computer modeling work to understand the impacts of the mountain pine beetle infestation on snowpack and runoff in the Big Thompson Watershed in Rocky Mountain National Park. Jennifer is conducting high resolution hillslope modeling for a site in Breckenridge, CO, to understand how heterogeneous forest land cover and a heterogeneous subsurface interact with selective beetle-killed trees to impact hydrology (snowpack and runoff). Partial summer salary was also provided to Prof Maxwell who is supervising students Bearup, Jefferson, Penn and co-supervising Mikkelson and supervising Dr. Engdahl.

Alexis Navarre-Sitchler: Partial summer salary to the Assistant Professor. Prof. Sitchler is supervising graduate student Pryhoda and co-supervising Bearup and Mikkelson who work on metals transport using field observations and laboratory experiments to better understand stream water quality as a result from the pine beetle infestation in Colorado's Rocky Moutains.

(c) The results achieved by the project

This past year has included laboratory, field and data analysis to further research the impact the pine beetle infestation has on water quality in the Rocky Mountain West. Column experiments were run to determine the impact pine needle leachate has on metal mobility, along with the gathering of field soil water samples under beetle impacted trees. The soil-water samples were used to determine if correlations existed between different metals and DOC content. These results were analyzed and written up in a paper that has been submitted to a peer-reviewed journal for publication. It is in its last stages of review at ESPI and should be published shortly.

We have also compiled all of the recent literature regarding bark beetle infestations and how they might impact local and regional water quality and quantity. This compilation has cumulated in a synthesis paper that explains how the bark beetle infestations are impacting water quality and quantity and what future research needs to focus on. This paper was published in the journal of Biogeochemisty.

Isotope data analysis was completed, including an end-member mixing study to determine the change in contributions to streamflow with bark beetle infestation. In this study, we hypothesized that MPB-induced changes in transpiration would impact flow partitioning differently than changes in interception or ground evaporation and would be reflected at the watershed scale as increased groundwater contributions to streamflow. Our analysis indicates increased groundwater contributions in the more heavily and recently impacted watersheds. Furthermore, water budget analysis suggests these changes are consistent with expectations of flux changes from transpiration loss. This work is currently under review with Nature Climate Change.

Sequential extractions on soils collected in 2012 were completed to determine changes in metal partitioning and mobility in MPB-impacted forests. Additional modeling analysis was also conducted in order to further interpret the lab/field results. This work found that changes in organic complexation and soil organic matter is the primary driver of the difference in metal mobility under trees during different stages of attack. This work is currently being prepared for submission.

Also, we used batch experiments to determine the leachate chemistry of pine needles from trees in three stages (the green, red and gray stages) of MPB infestation from Summit County, CO, a watershed currently experiencing the MPB epidemic impact of MPBs on water quality and ultimately groundwater geochemistry. Data analysis is ongoing, and concrete conclusions have not yet been made.

## Appendix F: School of Mines, Water Quality and Supply Impacts from Climate-Induced Insect Tree Mortality

This past year's modeling activities included development, testing, and refinement of integrated numerical models for the pine beetle impacted study site(s). The large scale ParFlow model domain (1km resolution) has been completed and is currently being tested with the CLM land-surface process model for the final, multi-year runs that will include the effects of land-cover change. This model was also used to assess the ability of integrated models to represent extreme flooding events, such as the catastrophic floods in Boulder, CO in September 2013. A smaller scale model (20m resolution) of a watershed within Rocky Mountain National Park has also been build that is being used to investigate how environmental tracers may be used to identify changes in the distribution of water in beetle impacted watersheds. Some preliminary theoretical work relating residence time and environmental tracer concentrations has been completed for this study which resulted in a publication. The final model for this small scale domain is currently running and investigates how the distribution of water changes given three different climate/land-cover conditions and the effects on tracer concentrations. The results of all the modeling studies are being compiled and prepared for publication in peer-reviewed journals.

We also have worked on the relationship between subsurface and surface characteristics, and surface fluxes like evapotranspiration (ET), one aspect that is significantly altered as a result of the mountain pine beetle infestation. We used ParFlow (PF), coupled with the Common Land Model (CLM), to model an idealized domain with homogeneous forest land cover and a heterogeneous subsurface representation of a Rocky Mountain watershed. Several scenarios with varying surface slopes and subsurface conditions were modeled to obtain annual ET distributions that were spatially-averaged at different resolutions. The average ET magnitude remained the same for each scenario regardless of the model resolution, while the standard deviation decreased with decreasing resolution. The relationship between hydraulic conductivity and ET was also found to vary with subsurface heterogeneity, anisotropy and conductivity magnitude; understanding these details, as well as the respective equations within PF-CLM that influence these relationships, is the focus of current research efforts.

**Publications:**


- Mikkelson KM, Bearup LA, Navarre-Sitchler AK, McCray JE, and Sharp JO (2013) Changes in metal mobility after needle drop in a bark beetle-infested forest. In Review. ESPI.

- Mikkelson KM, Bearup LA, Maxwell RM, Stednick JD, McCray JE, and Sharp JO (2013) Bark beetle infestation impacts on nutrient cycling, water quality and interdependent hydrological effects. Biogeochemistry. 115,1-21.

- Mikkelson KM, Dickerson E, McCray JE, Maxwell RM, Sharp JO (2013) Water-quality impacts from climate-induced forest die-off. Nature Climate Change 3, 218-222.

- Mikkelson KM, Maxwell RM, Ferguson I, McCray JE, and Sharp JO (2013) Mountain pine beetle infestation impacts: Modeling water and energy budgets at the hill-slope scale. Ecohydrology 6, 64-72.

- LA Bearup, RM Maxwell, DC Clow, and JE McCray Hydrological effects of forest transpiration loss in bark beetle-impacted watersheds. In review at Nature Climate Change

- Engdahl, N.B. and R.M. Maxwell (2014) Approximating groundwater age distributions using simple streamtube models and multiple tracers. Advances in Water Resources, ADWR2158, DOI: 10.1016/j.advwatres.2014.02.001

**Presentations:**

- Engdahl, N.B., and Maxwell, R.M. (2013) Realistic modeling of environmental tracer migration and composite age distributions in a pine beetle impacted watershed, Poster presentation H53F-1490, American Geophysical Union, Fall Meeting, December 9-13, 2013, San Francisco, CA.

- Engdahl, N.B., and Maxwell, R.M. (2013), Multi-scale modeling of the effects of landscape and climate changes on integrated hydrologic systems, Oral presentation T43-309-3, Geological Society of America, Annual Meeting, October 27-30, 2013, Denver, CO

- MK Pryhoda, AK Navarre-Sitchler, E Dickenson. Pine needle leachate chemistry from trees in three stages of mountain pine beetle attack. MODFLOW and More, Golden, Colorado, 2-5 June 2013.

- MK Pryhoda, AK Navarre-Sitchler, E Dickenson. Pine needle leachate chemistry from a mountain pine beetle infested watershed in Summit County, CO. GSA, Denver, Colorado, 27-30 October 2013.

- MK Pryhoda, AK Navarre-Sitchler, E Dickenson. Impact of pine needle leachate chemistry from a mountain pine beetle infested watershed on groundwater geochemistry. AGU, San Francisco, California, 9-13 December 2013.

- Lindsay A Bearup, RM Maxwell, C Penn, DW Clow, JE McCray. Connecting increased groundwater contributions to transpiration losses in bark beetle infested watersheds. AGU Fall Meeting, San Francisco, Calif., 9-13 December 2013.

- Lindsay A Bearup, KM Mikkelson, AK Navarre-Sitchler, RM Maxwell, JE McCray, JO Sharp. Metal Mobility in Bark Beetle-Infested Forests. GSA Annual Meeting, Denver, Colorado, 2013 Oct 27-30.

- Lindsay A Bearup, C Penn, RM Maxwell, DW Clow, JE McCray, JO Sharp. Unraveling the interconnection between hydrology and geochemistry in mountain pine beetle infested watersheds using stable isotopes and modeling. Poster at MODFLOW and More, Golden, Colorado, 2-5 June 2013.

- Lindsay A Bearup, RM Maxwell, DW Clow, JE McCray, JO Sharp. Interpreting watershed scale hydrological alterations from widespread mountain pine beetle infestation using stable isotopes. Poster at Hydrology Days, Fort Collins, Colorado, 25-27 March 2013.

- Colin A Penn, RM Maxwell, NP Engdahl, DW Clow. Effects of bark beetle infestation on hydrology and land-energy feedbacks in mountain headwaters. American Geophysical Union Fall Meeting, San Francisco, CA, 9-13 December 2013

## Appendix F: School of Mines, Water Quality and Supply Impacts from Climate-Induced Insect Tree Mortality

- Mikkelson KM, Ecohydrological impacts from climate-induced changes in land cover and vegetation in mountain environments, Co-chaired a session at the 2013 GSA annual meeting (October)

- Mikkelson KM, Will the bark beetle infestation affect water quality at water treatment plants in the Rocky Mountain West?, June 11th, 2013 AWWA conference in Denver, CO.

- Mikkelson KM , Will the bark beetle infestation affect water quality in the Rocky Mountain West?, May 14th, 2013 at the RMSWAWWA/RMWEA student conference at CSM, Golden, CO

- Mikkelson KM, Will the bark beetle epidemic impact water quality? Results from Colorado municipal water treatment facilities, February 18th, 2013 at the Institute of Arctic and Alpine Research, Boulder, CO.

- Jennifer L Jefferson, RM Maxwell. Understanding impacts of subsurface and surface heterogeneity on evapotranspiration in mountain pine beetle infested watersheds. Poster at AGU Fall Meeting, San Francisco, Calif., 9-13 December 2013.

- Jennifer L Jefferson, RM Maxwell. Understanding impacts of subsurface and surface heterogeneity on evapotranspiration in mountain pine beetle infested watersheds. GSA Annual Meeting, Denver, Colorado, 2013 Oct 27-30.